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Monitoring and Analysis of Hazardous Organics in Municipal Wastewater A Study of Twenty-Five Treatment Plants

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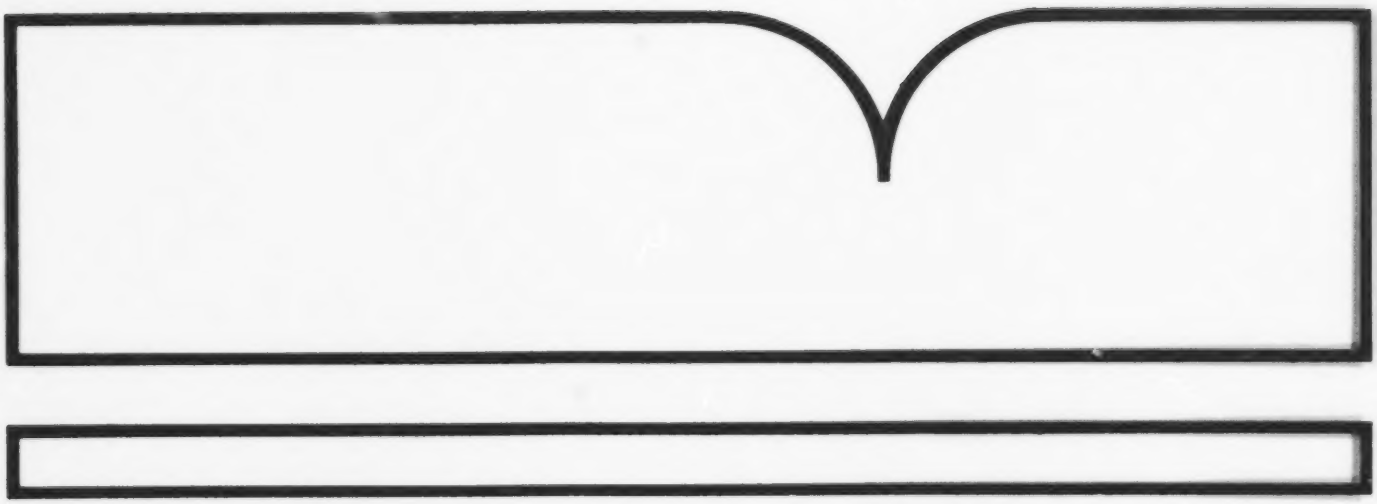

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MONITORING AND ANALYSIS OF HAZARDOUS ORGANICS IN MUNICIPAL WASTEWATER - A STUDY OF TWENTY-FIVE TREATMENT PLANTS

by

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16. ABSTRACT

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ABSTRACT

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MONITORING AND ANALYSIS OF HAZARDOUS ORGANICS IN MUNICIPAL WASTEWATER - A STUDY OF TWENTY-FIVE TREATMENT PLANTS

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INTRODUCTION

The modern industrial society manufactures, uses, and discharges to the environment tens of thousands of chemical compounds that amount to billions of pounds annually. It was long known that some of these chemicals were being discharged for treatment at publicly owned treatment works (POTW). Further, there was a strong presumption that some of these chemicals were incompletely removed and were being discharged with the effluents.

Until a few years ago the identification and quantification of the trace concentrations of organic chemicals in wastewater was beyond the capability of the analytical techniques of the time. As more sophisticated analytical instrumentation and techniques became available, they were quickly applied to wastewater analysis. In the early and mid 1970's wastewaters were analyzed for selected classes of compounds. For example, in 1971, Reichert, et al., (1) analyzed for polynuclear aromatic hydrocarbons; Schmidt, et al., (2) in 1971 and Lawrence and Toxine (3) in 1976 analyzed for PCB's. Not until the late seventies were analytical techniques sufficiently advanced to undertake to analyze wastewaters for more diverse classes of compounds. Then Chian and DeWalle (4) and Glaze, et al., (5) identified organic compounds which encompassed a wide range of classes of compounds.

A court imposed Consent Decree issued in 1976 (6) focused the attention of U.S. Environmental Protection Agency on a selected list of 129 compounds (now reduced to 127) including some 114 organic and 13 inorganic compounds. In the field of wastewater treatment, implementation of the Decree presented two immediate problems. First there was the need to develop the analytical

methods capable of analyzing raw wastewaters and sludges for the diverse classes of chemical compounds represented in the priority pollutant list; and secondly, there was the imperative need to establish a base of information on the numbers and amounts of compounds received at the POTW, the degree of removal accomplished by various treatment processes and the compounds and concentrations accumulated in the sludges.

To meet the above objectives, an EPA funded study was undertaken in June 1978, by the University of Washington and Georgia Institute of Technology that had two principal tasks. The first objective, which was crucial to completion of the second, was to develop and modify existing analytical methods to enable the analysis of raw wastewaters and sludge; and secondly, having the analytical techniques in hand, the objective was to obtain information on priority pollutants in wastewaters in a number of plants, nationally distributed, to provide a first-step overview of the status of priority pollutants in POTWs. This paper summarizes the results of the priority pollutants survey of 25 cities located throughout the United States. Results of the study are described in a report submitted to EPA by F. P. DeWalle, E. S. K. Chian, et al., entitled "Presence of Priority Pollutants in Sewage and Their Removal in Sewage Treatment Plants." (7)

Shortly after the initiation of the present study, a more extensive and comprehensive survey was undertaken by the USEPA Effluent Guidelines Division in Washington, D. C. The survey sampled 40 cities with each plant sampled for five consecutive days. Results of a portion of this study are described in two Interim Reports (8, 9).

ANALYTICAL METHODS DEVELOPMENT

State-of-the-art methodology has been developed to measure priority pollutants in wastewater and sludge at concentrations previously unattainable with standard methodology. Practical detection limits derived from minimum measured concentrations of priority pollutant organics were on the order of one µg/l except for pesticides where detection limits were near 10 ng/l.

Low molecular weight volatile compounds were measured using a modified Bellar/Lichtenberg procedure as shown in Fig. 1. In this method, the aqueous sample is spiked with one or more recovery/quantitation standards, diluted if necessary with purgeable-free water, and purged with a stream of organic-free helium. The gas stream is then passed through an inert adsorbent trap at room temperature where the entrained organics are retained. Upon completion of the purging, the trap is heated and back-flushed with organic-free helium to desorb the trapped organics. This sample stream is passed directly into a capillary GC column where it is cryotrapped at liquid nitrogen temperatures. When all of the sample has been desorbed and cryotrapped, the coolant is turned off and the cryotrap warmed with a flush of hot air. The GC or GC/MS analysis then ensues.

Recovery of selected volatile priority pollutants spiked into raw wastewater and into sludge from several different POTWs are shown in Table 1 and Table 2, respectively. Considerable variation in recoveries is evident for individual compounds in different wastewaters and sludges as well as for different compounds in the same wastewater or sludge. The recovery/quantitation standards consisting of deuterated volatile compounds were added to each survey sample before analysis. The standards were used to compute expected retention times to identify the priority pollutants and to correct for the variable recovery of similar priority pollutants. It was estimated that a single analyte quantitated against two internal standards would ordinarily vary by 5-10 percent.

Extractable priority pollutant organics were separated from aqueous samples in a stirred liquid-liquid continuous extractor developed at the University of Washington. The resulting extracts were further processed by gel permeation chromatography, florisil chromatography, and cesium silicate coupled chromatography to remove interferences and to fractionate the sample to facilitate analysis for individual compounds. Fig. 2 shows a simplified schematic for separation of extractable organics. Various solvent exchange and concentration steps have been omitted for clarity of presentation. Derivatization with diazomethane was used to improve the chromatographic behavior of the acidic compounds.

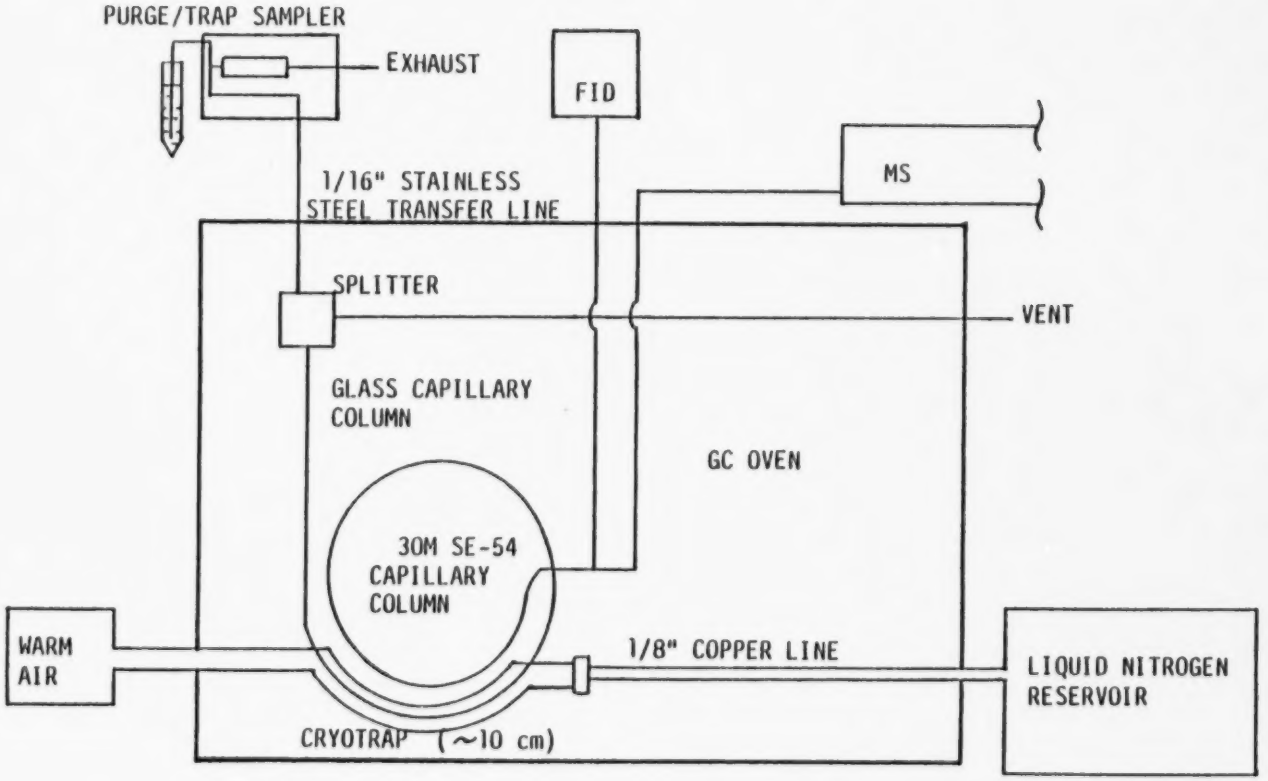


FIGURE 1. SCHEMATIC OF VOLATILE ORGANICS INSTRUMENTATION USING CRYOGENIC TRAPPING AND CAPILLARY GC/MS SEPARATION

TABLE 1. RECOVERY OF SELECTED VOLATILE PRIORITY POLLUTANTS FROM RAW WASTEWATER FROM FIVE POTW

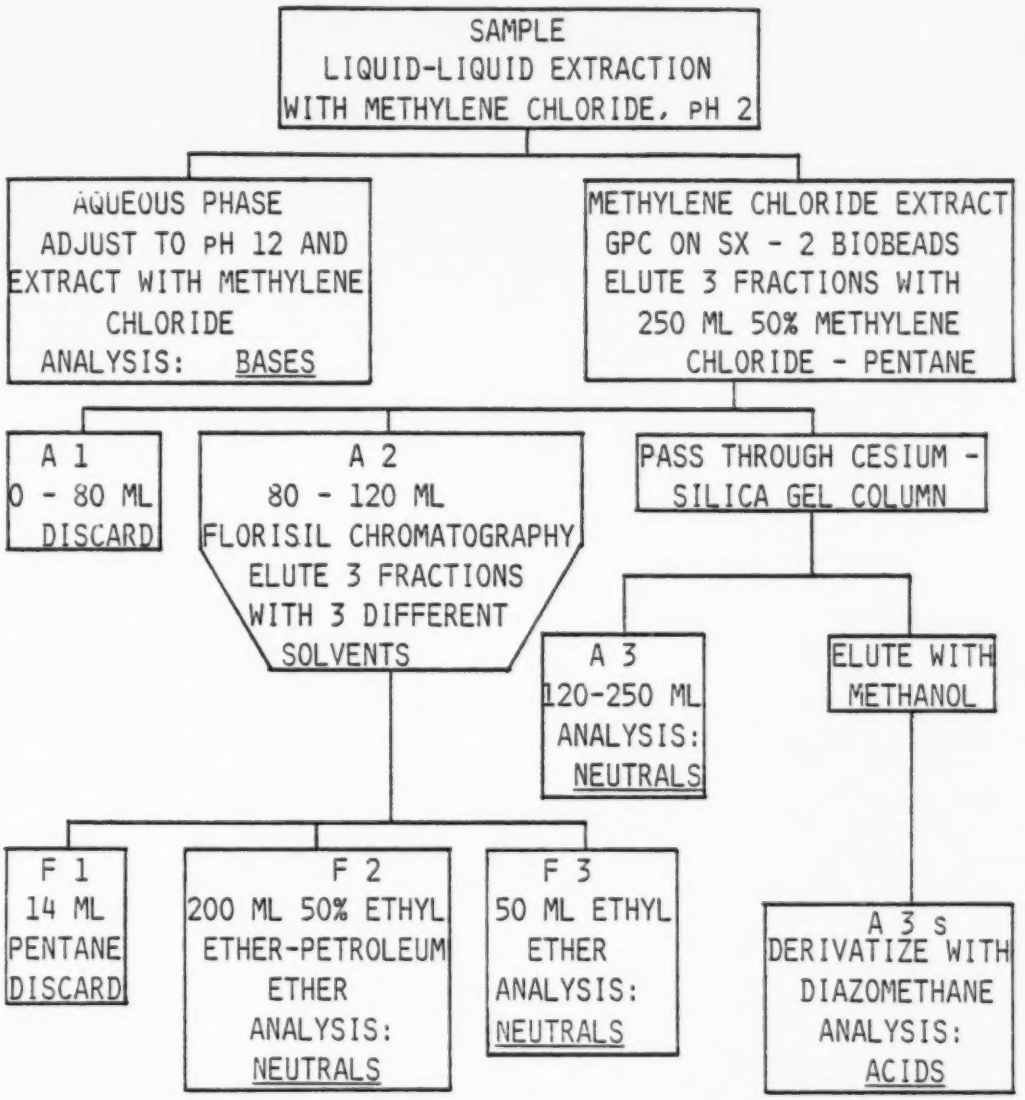
Pollutant Spiked at 20 ug/l	% Recovery for Listed POTW					Mean Recovery $\bar{x}$	Standard Deviation σ
	Roch-ester	Akron	Green-ville	Chatta-nooga	Seattle		
Ethene, 1,1-Dichloro	70	139	102	124	94	105	26
Methane, Dichloro-	223	243	59	133	ND	164	85
Methane, Trichloro-	106	117	72	192	43	106	56
Ethane, 1,2-Dichloro-	109	104	103	109	82	101	11
Benzene	89	109	97	81	90	93	10
Ethene, Tetrachloro-	67	67	90	240	110	115	72

ND = Not Detected

TABLE 2. RECOVERY OF SELECTED VOLATILE PRIORITY POLLUTANTS FROM SLUDGE FROM THREE POTW

Pollutant Spiked at 20 ug/l	% Recovery for Listed POTW			Mean Recovery $\bar{x}$	Standard Deviation σ
	Akron	Seattle	Tacoma		
Ethene, 1, 1-Dichloro-	73	155	49	92	55
Methane, Dichloro	80	123	188	130	54
Ethane, 1,2-Dichloro	89	142	130	120	27
Benzene	127	121	115	121	6
Ethene, Tetrachloro	80	66	75	74	7
Ethane, 1,1,2,2-Tetrachloro	53	213	119	128	80

FIGURE 2
EXTRACTION AND CLEANUP SCHEMATIC FOR PRIORITY POLLUTANTS



Analysis consisted of screening of each fraction by capillary GC-FID, subsequent recombination of the neutral components, capillary GC/MS analysis of the neutral and derivatized acid fractions, and GC/EC analysis of the neutral fraction to pick up low levels of PCB's and pesticides. The GC/MS data were analyzed by an automated data searching routine capable of applying both spectrum matching and GC retention time criteria for qualitative identification, and capable of either single-ion or multiple-ion quantitation.

As with the volatile analyses, the extractables require extensive use of blank and recovery samples to produce reliable quantitative data. Results of recovery tests for selected extractable compounds spiked into wastewaters and sludges are shown in Tables 3 and 4, respectively. In general, recoveries of extractables were lower than those of volatiles, particularly recoveries from sludges. Recoveries were also quite variable between different wastewaters for individual priority pollutants and for different priority pollutants in the same wastewater sample.

SELECTION OF CITIES

With some 20,600 municipal treatment systems in the United States, it was important that the small number of cities that would be sampled would constitute a reasonably representative sampling of the country. The number of compounds and concentrations in municipal wastewater was expected to be influenced by the amount and type of industrial waste discharged into the collection system. An important criterion for the selection of the cities was, therefore, based on an analysis of the industrial discharges to POTWs, differentiated by flow and type of industry.

Industry in the United States discharged a total of 14,144 billion gallons of water per year ($53 \times 10^{15} m^3$) (U.S. Census 1972) of which 56 percent or 7987 billion gallons/year ($30 \times 10^{15} m^3$) was untreated. The major portion was discharged to surface waters of various types but 7 percent or 990 billion gallons/year ($3.7 \times 10^{15} m^3$) was discharged to a public sewer. Not only was flow considered but also the type of industry since the degree of contamination

Table 3. Recovery of Selected Extractable Neutral Priority Pollutants From Spiked Raw Wastewater of Four Plants

Pollutant Spiked at 10 or 20 ug/l	% Recovery for Listed POTW					Mean Recovery $\bar{x}$	Standard Deviation σ
	Winston Salem	Seattle	Chatta-nooga (1st Sampling)	Chatta-nooga (2nd Sampling)	Peoria		
Nitrobenzene	65	75	73	29	59	60	18
Dimethylphthalate	54	59	80	16	61	54	23
2,6-Dinitrotoluene	68	69	42	30	67	55	18
Fluoranthene	28	11	29	21	36	25	9
Chrysene	19	14	54	30	64	36	22
Hexachlorobenzene	67	17	72	1	116	54	46

Table 4. Recovery of Selected Extractable Neutral Priority Pollutants From Spiked Sludge of Four Plants

Pollutant Spiked at 50 or 100 ug/l	% Recovery for Listed POTW				Mean Recovery $\bar{x}$	Standard Deviation σ
	Ft. Myers	Greenville	Peoria	Winston Salem		
Di-N-Butylphthalate	53	21	14	16	26	17
Fluoranthene	53	25	44	13	34	18
Naphthalene	66	72	58	23	55	21
Hexachlorobutadiene	55	13	75	18	40	29
Dimethylphthalate	68	49	84	26	57	25
2,4-Dinitrotoluene	58	37	NF	20	28	24

NF = Not Found

of the discharged water varies greatly with category of industry. Pretreatment before discharge by the industry was also taken into account.

The selection also considered the type of treatment process. Although the majority of the plants used activated sludge, three employed trickling filters and four used aerated lagoons or algal ponds. One of the POTW's practiced land spreading, and 12 of the 25 plants had combined sewers.

A further criterion was based on the size of the plants and geographical location. Plant sizes ranged from 3.5 mgd (13,000 m^3/day) to 309 mgd (1,170,000 m^3/day) while the percentage of industrial flow varied from 0 percent to 60 percent. A frequency distribution plot of plant size and percentage industrial flow, Figure 3, compares the 25-plant study with an EPA survey made in 1978 which inventoried 586 plants discharging > 5 mgd (18,925 m^3/day or more). The 25-city survey compares quite well with the much larger EPA survey especially when allowance is made for the additional criteria used in making the selection.

SAMPLING PROCEDURE

In the plant survey single 24-hr composite samples were taken from the influent, primary effluent and final effluent. In those plants that were using chlorination an additional sample of the final discharge was taken after chlorination. Grab samples were taken of the sludges of various types such as digested, primary, combined, etc. Nine of the cities were revisited for a second sampling, thus the survey consisted of 34 samplings of 25 cities. Some 30,000 chemical parameters were determined in the collected samples during the survey.

Since almost half of the priority pollutants are volatile to varying degrees - the more volatile compounds having half-lifes in open vessels of only 20-30 minutes - a sampler had to be devised which would circumvent losses of compounds by volatilization during the 24-hr compositing time. Based in part on a concept developed in our laboratory (10) a special sampler was constructed and used in the survey. Sample aliquots were taken proportional to flow and according to a delayed sequence whose timing was related to the

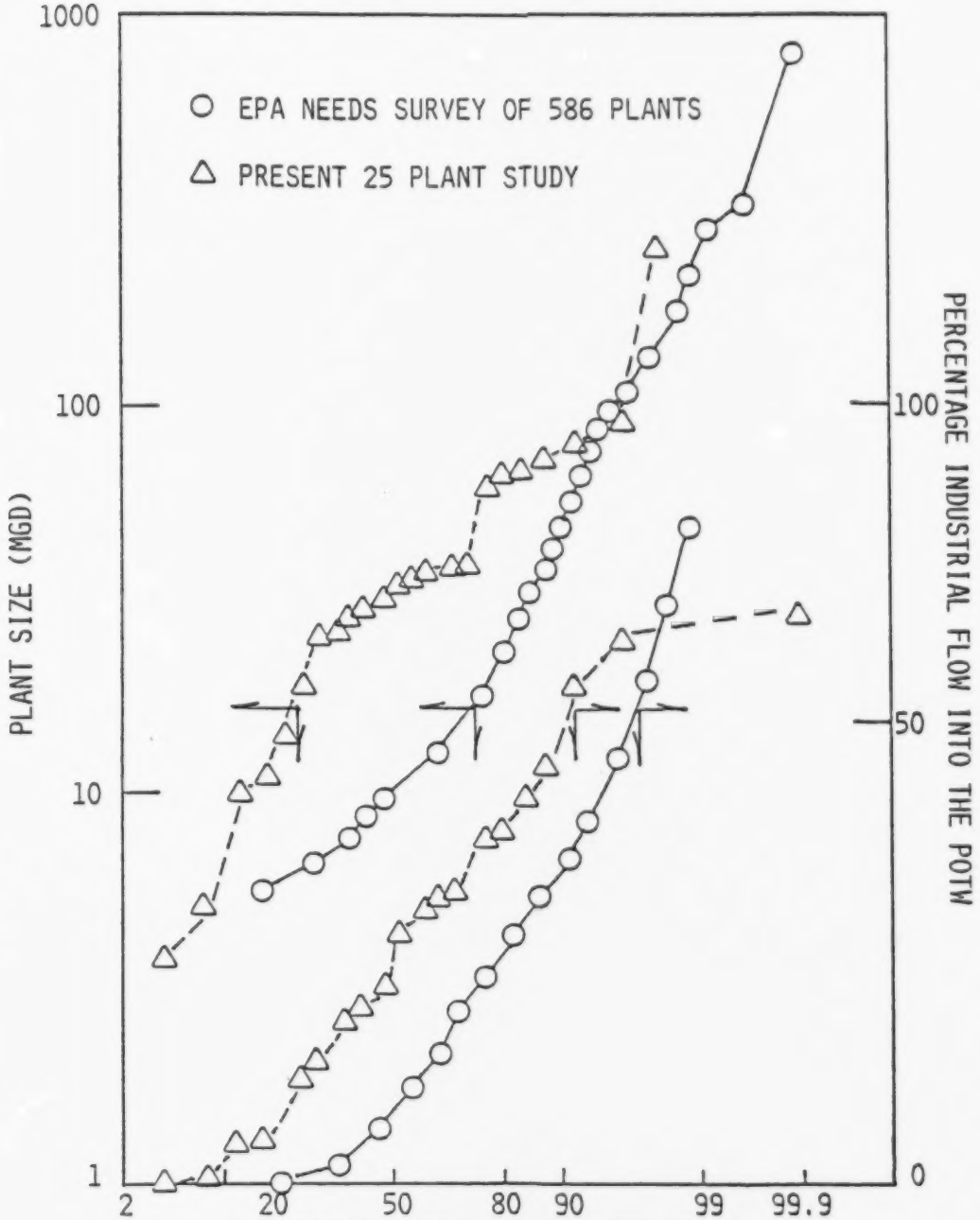


FIGURE 3. FREQUENCY DISTRIBUTION PLOT OF SIZE AND PERCENTAGE INDUSTRIAL INFLOW INTO POTWs

hydraulic detention in the plant. The sampler is described more fully by Tigwell, et al., (11).

DISCUSSION OF SURVEY RESULTS

Frequency of Occurrence and Removals in POTWs

Frequency histograms for the number of priority organic compounds found in individual wastewater and sludge samples from the different POTWs are shown in Fig. 4. Over a third of the raw wastewater samples (37%) contained between 30 and 40 organics at detectable concentrations while 83 percent of the samples contained between 20 and 50 organics. The maximum number found in any one sample was 57. The frequency distribution for the raw wastewaters is relatively symmetrical.

The final discharge samples are skewed to the lower end in number of organics detected. Forty-one percent of the samples had between 10 and 20 priority organics. Only 6 percent had more than 40 organics present. Three quarters of the sludge samples (75%) had between 20 and 40 organics detected. Again the distribution for the sludge samples is skewed toward the low end.

Figure 5 compares the number of priority organics detected in each raw wastewater sample with the total concentration of all priority organics in the sample. Each point represents one 24-hour composite sample at a POTW. The total concentration of priority organics in a sample was calculated by summing the concentrations of the individual priority organics measured in the sample. The majority of samples from the raw wastewaters from the different cities contained less than 1000 µg/l (1 mg/l) of priority organics. Also as previously shown in Figure 4, the number of compounds detected tends to cluster between 20 and 50. For those samples containing more than 1000 µg/l of priority organics, the data indicate that about the same number of organics are present at higher concentrations rather than a larger number of organics at normal concentration levels. It is obvious from the figure that there is no defined relationship between number and total concentration of priority organics over all the POTWs.

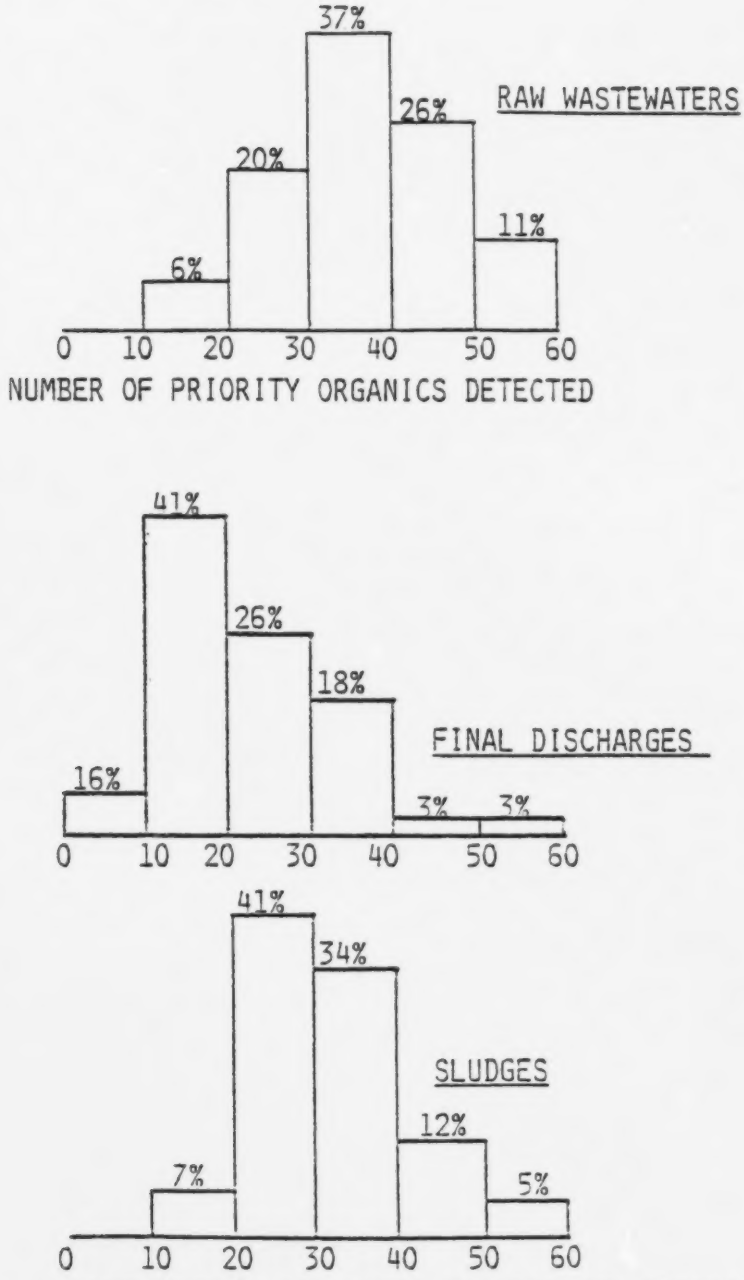


FIGURE 4. DISTRIBUTION OF NUMBER OF PRIORITY ORGANICS DETECTED IN INDIVIDUAL WASTEWATER AND SLUDGE SAMPLES

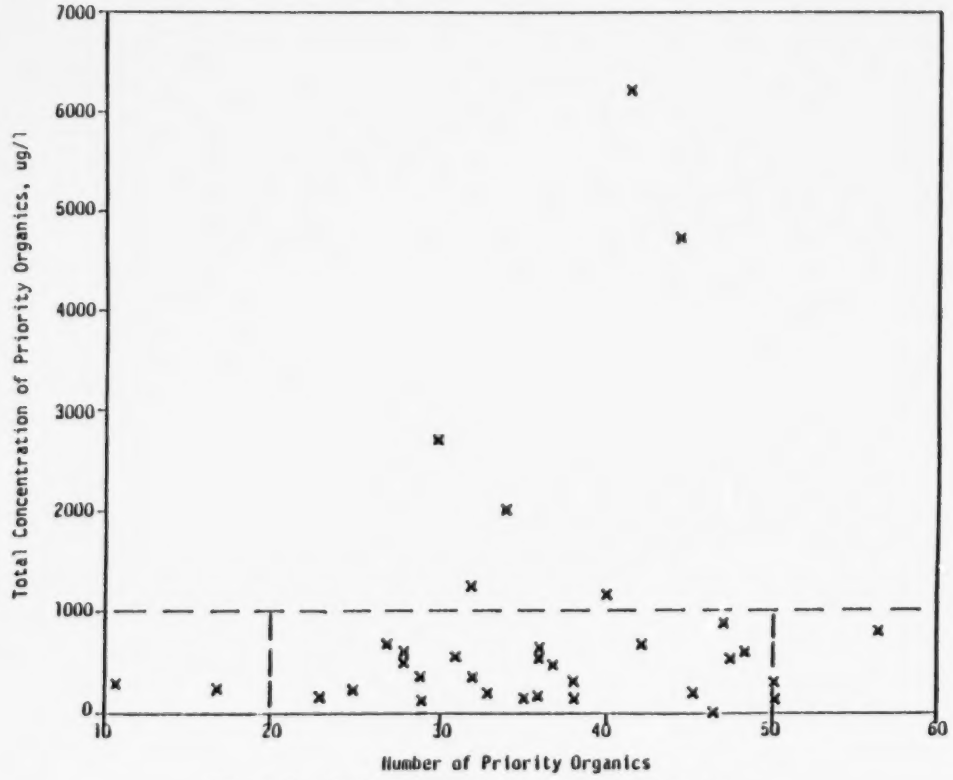


Figure 5. Total Concentration of Priority Organics VS. Number of Compounds in Raw Wastewater Samples

Since many priority organics in municipal wastewaters are believed to be from industrial sources, the number of priority organics in raw wastewaters was plotted against percent industrial flow as shown in Figure 6. The solid line is the least squares fit for the points enclosed by the two dashed lines. There appears to be a generally increasing trend in number of compounds found with increasing industrial flow. The coefficient of determination of this fit is, however, only 0.2.

No correlation was observed between total concentration of priority organics and percent industrial flow. This is most probably due to the varying nature of the industries and different levels of pretreatment provided in the cities surveyed.

Table 5 shows the variation in number of individual organics detected in raw wastewaters and final discharges at three selected frequencies above detection limits and concentrations of 1, 10, and 50 µg/l. A total of 83 different organics were detected in raw wastewater samples from the survey while 79 different organics were detected at least once in the final discharge samples. Some 54 different specific priority organics appeared in at least 25 percent of the raw wastewater samples while 36 different organics were detected in at least 25 percent of the final discharge samples. Note that this is not the same as saying that 25 percent of the final discharge samples had 36 organics present since the 36 in question could be occurring in different samples.

The raw wastewaters contained 80 different organics that exceeded 1 µg/l at least once, 56 that exceeded 10 µg/l at least once and 31 that exceeded 50 µg/l at least once. The final discharges contained only 13 different organics that exceeded 50 µg/l at least once. The final discharges also contained only 13 different organics that appeared above detection limits in 50 percent or more of the samples. No individual organics were found to exceed 50 µg/l in 50 percent of either the raw wastewaters or final discharges.

The numbers of individual priority organics found in sludges at three selected frequencies are shown in Table 6. The sludge samples represent 9 raw primary sludges, 8 raw waste activated sludges, 5 raw combined sludges, 18

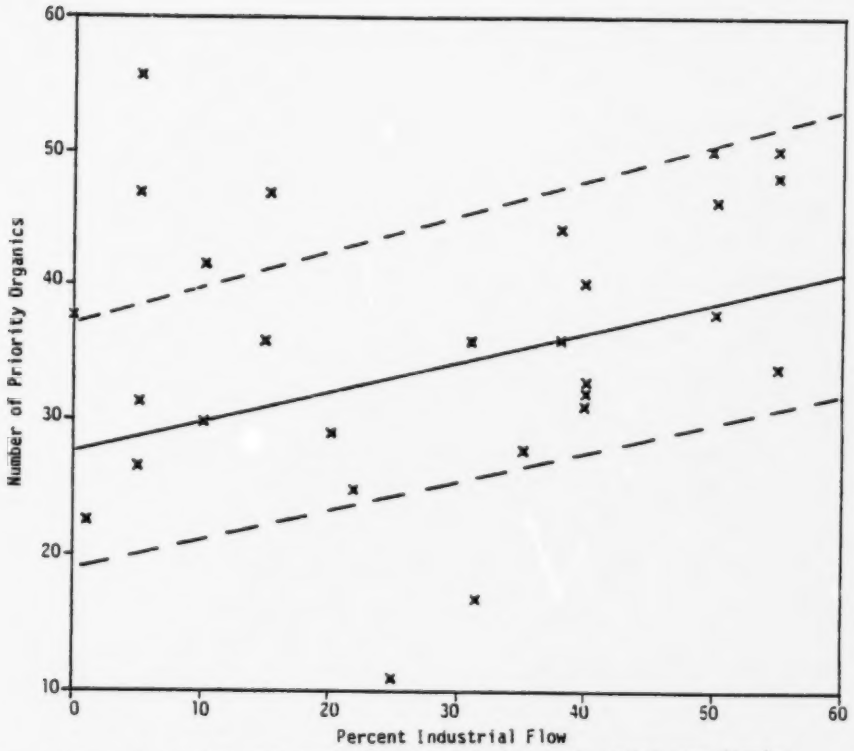


Figure 6. Number of Priority Organics Detected in Raw Wastewater Samples VS. Percent Industrial Flow

TABLE 5. NUMBER OF INDIVIDUAL PRIORITY ORGANICS FOUND IN RAW WASTEWATER AND FINAL DISCHARGES

Concentration, µg/l	Number Found in Indicated % of Samples					
	>0%		≥25%		≥50%	
	Raw	Final	Raw	Final	Raw	Final
>Detection Limit	83	79	54	36	32	13
>1	80	64	26	14	18	7
>10	56	37	14	3	10	0
>50	31	13	3	1	0	0

TABLE 6. NUMBER OF INDIVIDUAL PRIORITY ORGANICS FOUND IN SLUDGES

Concentration, mg/kg	Number Found in Indicated % of Samples		
	>0%	≥25%	≥50%
>Detection Limit	82	48	29
>1	72	22	7
>10	47	6	1
>50	33	1	0

digested sludges, and 2 heat-treated sludges. Eighty two compounds were detected at least once, 48 were detected in 25 percent of the samples and 29 were found in half of the samples. Thirty-three compounds were found at least once in concentrations greater than 50 mg/kg but only one compound was found in 25 percent of the samples at that concentration.

Table 7 summarizes the most frequently found compounds at levels of 1, 10, and 50 µg/l in raw wastewaters and final effluents, and at levels of 1, 10, and 50 mg/kg for sludges. These include all of the compounds found above 1 µg/l (or 1 mg/kg) at least 80 percent of the time in raw wastewaters and at least 50 percent of the time in final discharges and sludges. The total number of priority organics meeting these selection criteria is only 15. Five are chlorinated methane or ethane derivatives, four are substituted benzenes, two are PAH's while four are phthalates.

The ranges of total concentrations of nine classes of priority organics in individual raw wastewaters and final discharges are shown in Figure 7. The upper bar for each class, labeled R, is for raw wastewater; the lower bar, labeled F, is final discharge. Identified on each bar are the minimum reported discrete value, the 25th percentile, the median concentration, the 75th percentile, and the maximum reported value for the selected class and type of sample. Because of the wide range of values, a logarithmic concentration scale was used. Total concentrations generally ranged over 3 to 4 orders of magnitude with interquartile ranges (25% to 75%) ranging between 1 and 2 orders of magnitude. The positions of the medians indicate that the concentration distributions are skewed to the left with most of the values at the lower end of the concentration range. Final discharge ranges were always lower than raw wastewater ranges, however, no conclusions regarding percent removals should be drawn from Figure 7 since the data do not segregate influent-effluent pairs from a single plant.

Figure 8 was prepared from single plant influent and effluent data pairs to show the interquartile ranges of percent removals for the same 9 classes of priority organics. The left end of each bar represents the 25th percentile while the right end is the 75th percentile of the data set. High variability was observed for the methanes, ethanes, and pesticides. The wide range of

TABLE 7. MOST FREQUENTLY DETECTED COMPOUNDS IN RAW WASTEWATER, FINAL DISCHARGE AND SLUDGE SAMPLES

	Percent Occurrence at Indicated Concentration								
	Raw Wastewater			Final Discharge			Sludge[a]		
Compound	≥ 1 ug/L	≥ 10 ug/L	≥ 50 ug/L	≥ 1 ug/L	≥ 10 ug/L	≥ 50 ug/L	≥ 1 mg/kg	≥ 10 mg/kg	≥ 50 mg/kg
Methane, dichloro-	83	57	33	79	41	28	41	12	3
Methane, trichloro-	74	26	3	55	6	0	3	0	0
Ethane, 1,1,-trichloro-	90	61	16	53	22	6	5	3	0
Ethene, trichloro-	90	61	19	47	16	3	26	9	3
Ethene, tetrachloro-	94	65	26	77	19	3	27	8	3
Benzene, 1,4-dichloro-	83	37	6	38	6	0	36	18	5
Ethylbenzene	87	23	13	13	3	0	33	3	0
Toluene	84	61	23	45	17	3	59	35	11
Phenol	86	66	31	38	6	3	63	25	13
Naphthalene	86	37	11	24	3	0	65	33	15
Phenanthrene	57	9	0	15	3	0	60	20	8
Phthalate, diethyl	91	57	17	62	29	0	43	23	13
Phthalate, di-n-butyl	89	60	9	85	18	3	63	25	13
Phthalate,bis(2-ethylhexyl)	86	69	20	76	38	6	75	63	25
Phthalate,butylbenzyl	77	60	11	32	15	0	50	35	18
All Others	< 80	< 60	< 20	< 50	< 20	< 10	< 50	< 25	< 15

[a] Expressed on dry solids basis.

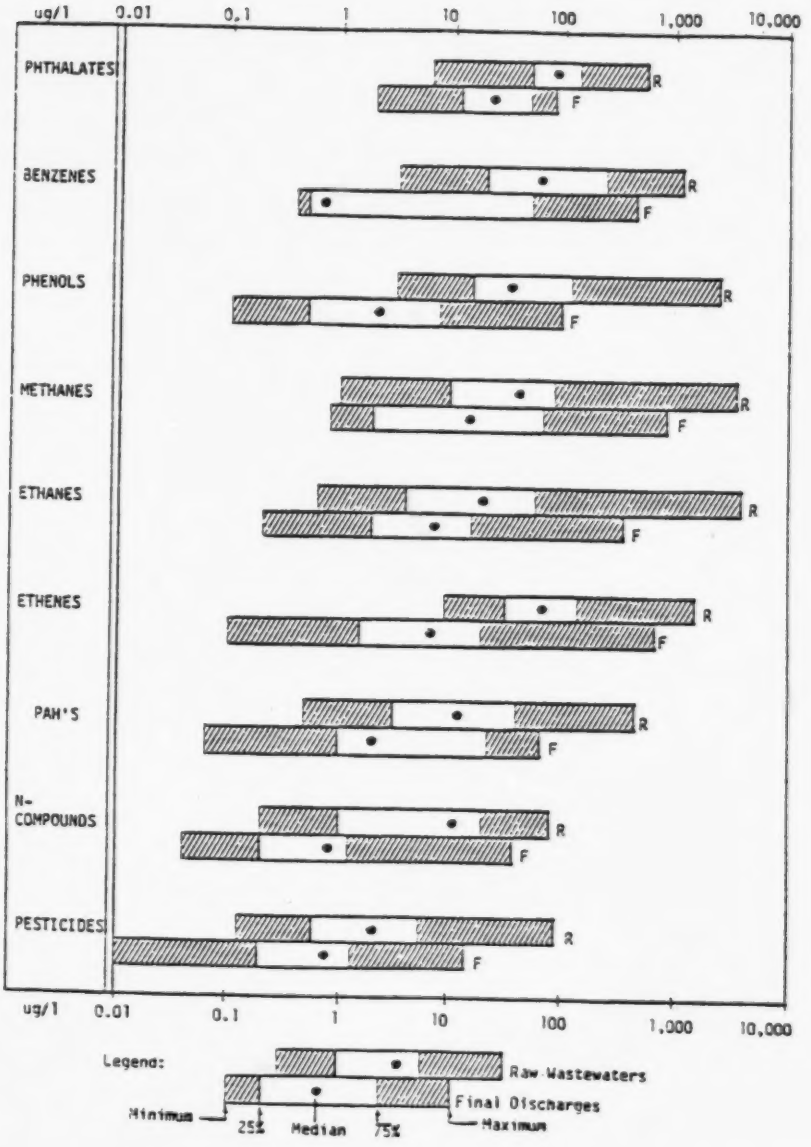


Figure 7. Ranges of Total Concentrations of Nine Classes of Organics in Raw Wastewaters and Final Discharges

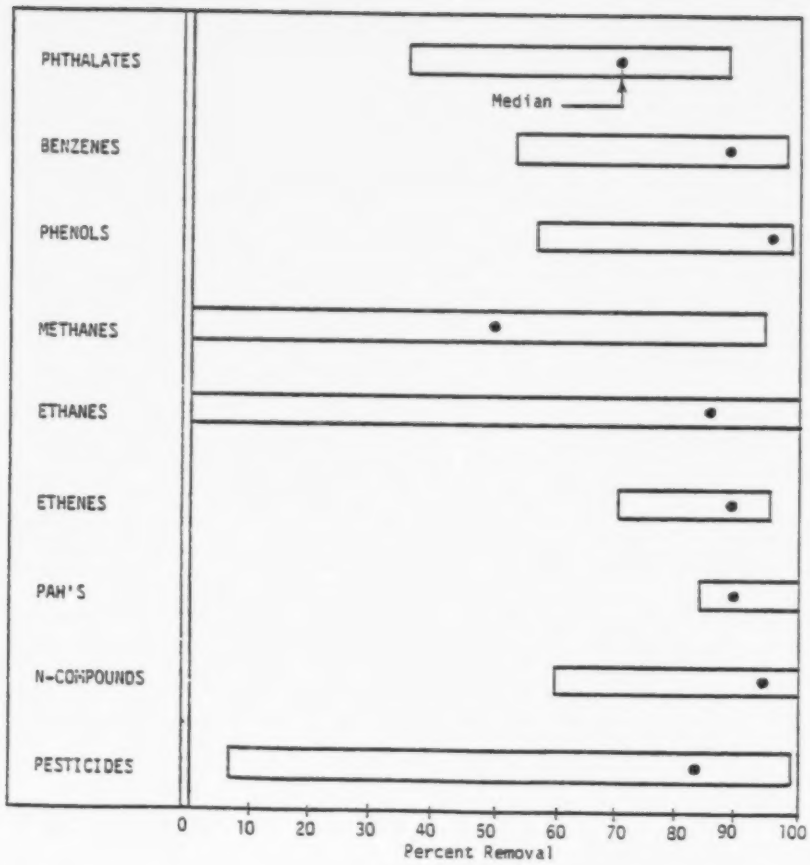


Figure 8. Interquartile Ranges of Percent Removals for Classes of Priority Organics

removals for the former two classes can be explained by the production of chlorinated methanes and ethanes in final discharges during disinfection with chlorine. In fact, negative removals are sometimes observed where final discharge concentrations exceed those in raw wastewater. The wide range in pesticide removals is most likely due to the low concentrations of pesticides near the analytical detection limits in wastewaters and the attendant analytical errors involved. The use of 24-hour composites for calculation of percent removals does not necessarily reflect the long-term removals at the surveyed plants and will cause some scatter in the data. Median removals for benzenes, phenols, ethanes, ethenes, PAH's, nitrogen-containing-compounds, and pesticides were all greater than 80 percent. Of these, the ethenes and PAH's have the most consistent range of removals.

Figure 9 was prepared to determine if there was any relationship between the total concentrations of priority organics in the raw wastewaters and in final discharges. Final discharge concentrations were plotted against raw wastewater concentrations for 31 plant visits. The best fit curve through these data was found to be a power relationship with a coefficient of determination of only 0.3. Again, the fact that wastewater samples were only 24-hour composites with very different compositions from plant to plant would not lead one to expect a quantitative relationship between gross concentrations in and out of different POTWs. Several individual compounds were also tested but no consistently strong relationship could be discerned between influent and effluent concentrations.

Because analysis for specific priority pollutant organics is both time-consuming and expensive, there have been a number of attempts to relate concentrations and removals of priority organics to other more common analytical parameters. Figure 10 shows a plot of percent priority organics remaining after treatment versus the percent COD remaining. As observed from the figure, COD removal is not a good predictor of priority organics removal. The coefficient of determination of the least squares power function fitted to these data was only 0.1.

Paired influent-effluent data from 34 samplings were classified as being from secondary plants (23 events) or from tertiary plants (11 events). The

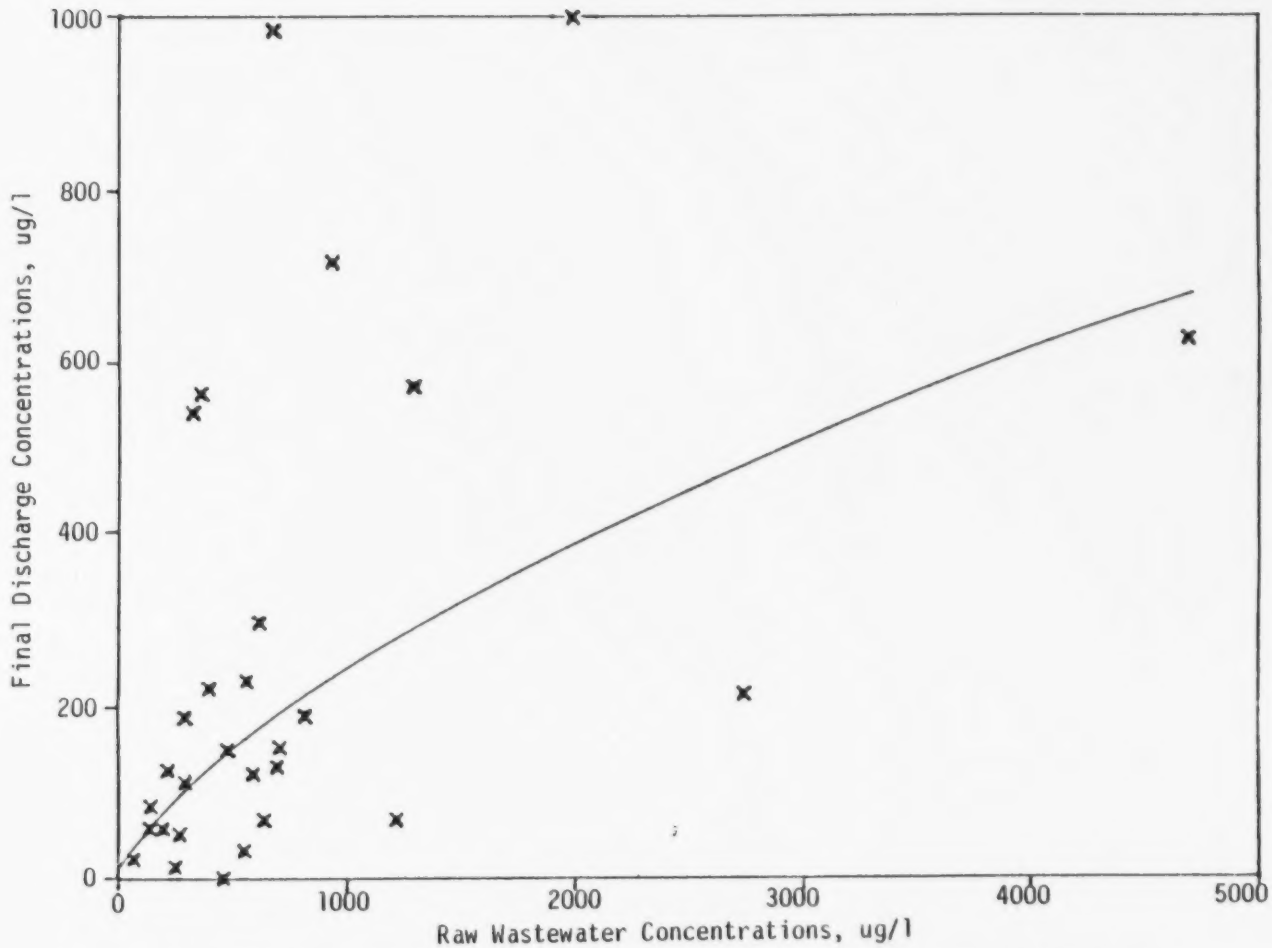


Figure 9. Final Discharge vs. Raw Wastewater Concentration of Priority Organics

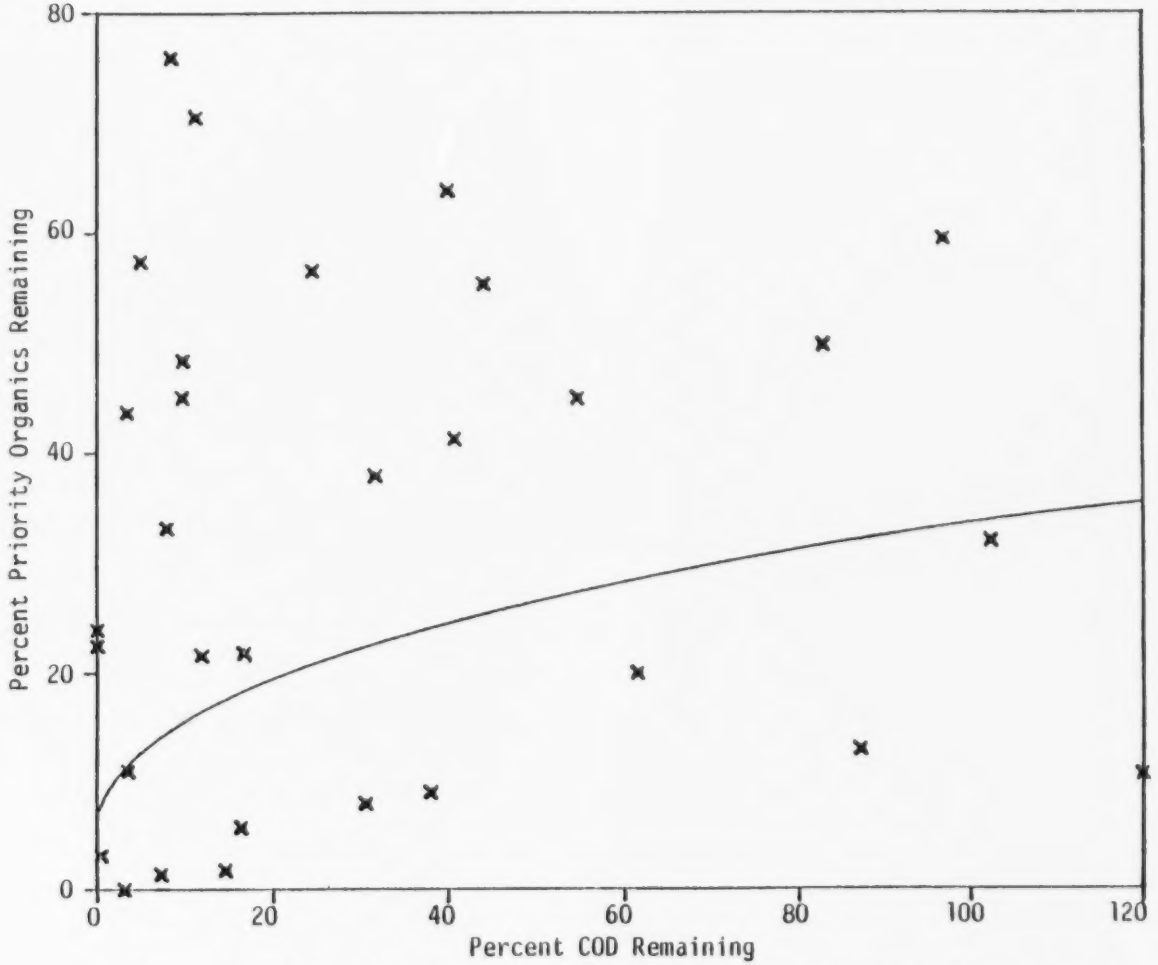


Figure 10. Percent Priority Organics Remaining vs. Percent COD Remaining

tertiary data were from eight separate plants consisting of either activated sludge, trickling filters, or lagoons followed by either trickling filters (1 plant), gravity filters (2 plants), lagoons (3 plants), RBC (1 plant), or land application (1 plant). On average, the percent reduction in number of compounds detected between the influent and effluent in secondary systems was 28 percent (σ = 10%); for tertiary systems, 36 percent (σ = 19%). This difference in reduction in numbers of compounds cannot be called significant at either the 5 percent or 10 percent confidence levels. In terms of total concentrations of priority organics, secondary plants had an average of 51 percent removal (σ = 42%) while tertiary plants had an average of 67 percent removal (σ = 44%). Again, because of the high variability between plants, it was not possible to call this difference in percent removal significant at either the 5 percent or 10 percent level.

Production of Chlorinated Organics

Where chlorination was practiced, effluent samples before and after chlorination were examined for both the total number and total concentration of potential chlorination products. These included 20 chlorinated aliphatics, 6 chlorinated benzenes, and 4 chlorinated phenols. On average, less than one (0.73) additional compound was detected after chlorination than before (σ = 3.2) and total concentrations of the selected compounds increased 68 µg/l(σ = 218). Given the variability of these results, it was not possible to discern at 5 percent or 10 percent confidence levels that chlorinated organics were being produced by chlorination.

Significance of Priority Organics in Final Discharges

Concentrations of individual priority organics and toxic metals in final discharges were compared with proposed USEPA Water Quality Criteria to evaluate their significance in terms of potential damage to human health or aquatic life. Water quality criteria were taken from values published in the November 28, 1980 Federal Register. (12) They were divided into the following four categories based on designated receiving water uses:

1. Protection of Freshwater Aquatic Life

Chronic or maximum 24-hour average concentrations were used for 66 compounds. For 40 others with no chronic limits listed, the acute or never to be exceeded concentrations were used. For certain metals whose toxicity depended on water hardness, a hardness of 100 mg/l $CaCO_3$ was assumed. Limits based on algal toxicity were excluded.

2. Protection of Saltwater Aquatic Life

Chronic or maximum 24-hour average concentrations were listed for 40 compounds. Another 60 had only acute or never to be exceeded levels listed. Again, limits based on algal toxicity were excluded.

3. Recreation (Fishing)

Limits for 86 compounds, based on the protection of human health for consumption of contaminated fish, were used. Sixty-two of these were potential human carcinogens for which no absolutely safe level could be established. In these cases, limits based on an incremental increase of cancer risk over a lifetime of 1/1,000,000 were used. Criteria based on organoleptic data were excluded.

4. Public Water Supply

Limits for 98 compounds were included. These were developed for protection of human health based on consumption of both fish and water. Sixty-two compounds were suspected carcinogens for which a risk level of 1/1,000,000 was used. Again, criteria based on organoleptic data were excluded.

With the above effluent samples and water quality criteria, determinations were made on a plant by plant basis of how many and what types of compounds were exceeding different types of criteria under different dilutions, or ratios, of "clean" receiving water flow to plant discharge flow. The dilutions examined--15:1 for freshwater aquatic life, recreational fishing and

water supply and 100:1 for saltwater aquatic life--were chosen to be representative for the designated use being analyzed.

The summary results of this analysis are shown in Table 8. The table shows the number of plants having one or more pollutants that exceed proposed water quality criteria for each water use, the number of different pollutants exceeding the proposed criteria for each use, the average number of criteria exceeded per plant and the individual pollutants most frequently involved. From these data, the following trends can be discerned:

1. Essentially all of the treatment plants have pollutants that exceed at least one proposed criterion for Freshwater Aquatic Life, Recreation (Fishing), and Water Supply.

2. Many pollutants exceed criteria at one or more plants. However, the "average" plant has only one to seven pollutants exceeding criteria at the selected dilutions.

3. Protection of Saltwater Aquatic Life is the designated use most readily attained with the pesticides most frequently exceeding criteria.

4. Several toxic metals and cyanide are problematic in attaining Freshwater Aquatic Life Criteria. The carcinogens arsenic and beryllium are problematic for Recreation (fishing) and Water Supply criteria.

5. Mixtures of several different PAH's in secondary effluents exceed Recreation (fishing) and Water Supply criteria. Since these criteria are generally 0.003 µg/l to 0.03 µg/l, which is below the normal detection limit of PAH's, detection of PAH's likely means exceeding criteria as well.

6. On average, two chlorinated methanes exceeded Water Supply criteria.

TABLE 8. PRIORITY POLLUTANTS EXCEEDING PROPOSED WATER QUALITY CRITERIA

Criteria and Dilution	Number of Plants with Pollutants Exceeding Criteria	Number of Different Pollutants Exceeding Criteria	Average Number of Pollutants Per Plant Exceeding Criteria	Compounds Most Frequently Exceeding Criteria (Number of Plants)
Freshwater Aquatic LIfe 15:1	25	19	3 Inorganics 1 Pesticide	Cadmium (19), Silver (14), Mercury (13), Cyanide (12), Lead (10), Copper (9), DDT (7), Heptachlor (7)
Saltwater Aquatic Life 100:1	13	11	1 Pesticide	DDT (6), Heptachlor Epoxide (3), Heptachlor (2), Endrin (2), Copper (2), Cyanide (2)
Recreation (Fishing) 15:1	24	19	1 Inorganic 2 Pesticides 1 PAH	Arsenic (18), Heptachlor (11), Aldrin (10), Heptachlor Epoxide (7), DDT (7), Dieldrin (6), Beryllium (5), Phenanthrene (5)
Water Supply 15:1	25	40	2 Inorganics 2 Pesticides 1 PAH 2 Aliphatics	Arsenic (18), Beryllium (17), Dichloromethane (17), Heptachlor (11), Aldrin (10), Chloroform (10), BHC-b (8), DDT (7), Heptachlor Epoxide (7)

With regard to other classes of compounds, no general pattern emerges. It should be noted that many of the carcinogens, such as the chloroalkyl ethers, PCB's, nitrosamines, benzidines, and PAH's, have proposed water quality criteria in the range of 10^{-3} to 10^{-6} µg/L; these are well below the nominal detection limits of 1 µg/L for the analytical screening techniques used in the plant survey. These compounds could therefore exceed the water quality criteria without being detected in any sample.

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